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Volatile Fluoro Compounds

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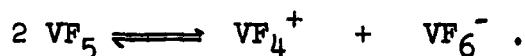April, 1963

University of British Columbia

Part 1.

The Density, Viscosity, and Surface Tension
of Vanadium Pentafluoride

by R. G. Cavell and H. C. Clark

The high specific conductivity and Trouton's constant[1,2] suggest that vanadium pentafluoride is associated, and also that it ionises:

$$2\ VF_5 \rightleftharpoons VF_4^+ + VF_6^- \ .$$

Intermolecular association in covalent fluorides seems to occur through fluorine bridge bond formation; thus the F^{19} nuclear magnetic resonance spectrum of antimony pentafluoride indicates the formation of polymeric chains through such fluorine bridge bonds[3]. The extent of intermolecular association in a liquid appears to be reflected by properties such as surface tension and viscosity, and these have now been determined for liquid vanadium pentafluoride.

Experimental: Vanadium pentafluoride was prepared by the direct fluorination of powdered vanadium metal as previously described[1]. Density: A silica dilatometer, calibrated with mercury, was filled in vacuo with vanadium pentafluoride, and sealed. The volume of liquid was determined at approximately $5°$ intervals over the temperature range $20\text{-}45°$, with both increasing and decreasing temperature to check the reproducibility. The results are shown in the following tables:

Experiment 1.

t($^{\circ}$c) ..... 20.0 25.2 30.2 34.7 39.8 44.9 30.1 24.3 20.4 26.

ρ(g.cc.$^{-1}$). 2.508 2.489 2.478 2.457 2.435 2.414 2.470 2.489 2.500 2.48

Experiment 2.

t($^{\circ}$c) ..... 20.6 25.3 30.9 35.1 40.4 45.0 37.7 30.3 25.0 20.

ρ(g.cc.$^{-1}$). 2.491 2.474 2.459 2.444 2.424 2.406 2.435 2.462 2.479 2.49

The average expression for the density from two experiments, includ-
ing standard deviations, is ρ = 2.483 ($\pm$ 0.004) - 0.00349 (t-25°)
($\pm$0.00008) g. cc^{-1}, and the average coefficient of expansion is
$\frac{1}{V}$ $^{dV}/_{dt}$= 1.472 $\pm$ 0.025 deg^{-1}.

Viscosity: A Pyrex viscometer was used, consisting of a 15 cm.
length of 1 mm. capillary tubing joining an upper bulb of around
1 ml. capacity to a lower bulb of around 2 ml. capacity. An
8 mm. diameter tube, parallel to the capillary, was joined to the
top of the large reservoir and was fitted at the top with a metal
tap (Hoke type 431). A second tap provided a connection between
the two arms of the viscometer and thus permitted a variation in
the relative pressure between the arms. After the apparatus had
been "baked" in vacuo at 100° for two days, approximately 2 ml.
of vanadium pentafluoride was distilled in. The viscometer was
then sealed to a vacuum line through which a variable pressure of
dry nitrogen could be provided. With the tap connecting the two
arms of the viscometer closed, the application of nitrogen pressure
through the main tap forced the liquid into the upper reservoir.
The pressure between the two arms was then equalised, and with
the viscometer immersed in a thermostated water bath, the liquid
was allowed to flow under the influence of its hydrostatic

pressure into the lower reservoir. Where possible, several measurements of the flow time at each temperature were made. Considerable difficulty was caused by the volatility of vanadium pentafluoride which seriously limited the accessible temperature range, and also caused some of the pentafluoride to distil out of the viscometer when the pressure of nitrogen was reduced between each measurement. The latter step was necessary in order to avoid using increasingly greater pressures of nitrogen. Despite extreme precautions, some decomposition of the pentafluoride also occurred, as shown by a gradual darkening of the liquid during the experiment. The viscometer was calibrated with concentrated sulphuric acid, this being the only liquid of reliably known viscosity which was at all close to matching the density and viscosity of vanadium pentafluoride. The results are shown in the following table. The number of determinations at each temperature is given in brackets beside the average value of the viscosity.

$t(^{\circ}C)$	25.35	25.45	31.9	32.0	27.3	27.3
η(centipoise)	124.2(3)	125.7(2)	86.8(1)	76.4(3)	110.4(1)	120.0(1)

From eleven measurements of flow time at temperatures in the range 25.35 - 32.00°, the viscosity of vanadium pentafluoride can be expressed by the equation $\eta = 124 - 7.2\ (t-25^{\circ})$ centipoise. Considering the above sources of error, the viscosity given by this equation probably has a maximum error of $\pm$ 20%.

Surface Tension: In one experiment (i), the capillary rise in three capillaries ranging from 0.5 - 1.5 mm. internal diameter was measured, and in another experiment (ii), a differential capillary tensiometer[4] was used. The surface tension, γ, was

calculated from the expression $\gamma = \frac{f \Delta h}{\rho}$, where f = apparatus factor, Δh = difference in level of liquid in each of two capillaries, or the height of liquid in the capillary above the level in the reservoir, and ρ = density of the liquid. The apparatus factor (f) was determined for each apparatus by measuring Δh for a liquid of known density and surface tension such as water or benzene. Measurements were made over the temperature range 24.5 - 37.0°, and the results for the two experiments are shown in the following table.

	(i)			(ii)		
t(°c).........	24.5	29.7	34.8	24.75	29.5	37.0
γ(dynes cm^{-1}).	18.35	18.0 17.75	16.75	18.1	17.15	16.5

Least squares analysis of the data for both experiments gives for the surface tension of vanadium pentafluoride, γ = 18.2 - 0.142 (t-25°) dynes cm^{-1}, with a probable error of $\pm$ 0.2 and a standard deviation of $\pm$ 0.3.

Discussion: Ruff and Lickfett[5] have previously reported the density of solid vanadium pentafluoride as being 2.1766 g. cc^{-1} at 19°. This is clearly in error, since liquid vanadium pentafluoride has a higher density, and a very marked contraction occurred when the liquid was frozen in the dilatometer. Ruff and Lickfett's erroneous result was probably due to extensive hydrolysis of their samples of the pentafluoride to the oxytrifluoride. The present value for the density of liquid vanadium pentafluoride at 25°, 2.483 g. cc^{-1}, is comparable with the densities[6] of antimony pentafluoride (2.99 g. cc^{-1}), bromine trifluoride (2.80 g. cc^{-1}), bromine pentafluoride (2.46 g. cc^{-1}), and iodine pentafluoride (3.19 g. cc^{-1}).

Although the equation obtained is not exceptionally accurate, the viscosity of vanadium pentafluoride is clearly much higher than for most liquid fluorides. Thus, for bromine trifluoride the viscosity at 25° is 2.22 centipoise, and for iodine pentafluoride 2.19 centipoise[6]. Only antimony pentafluoride with a viscosity of 460 centipoise[7] at 25° has a higher viscosity than VF_5, and it has been shown[3] that antimony pentafluoride is associated into fluorine bridged polymers. The high viscosity of vanadium pentafluoride thus indicates considerable polymeric association in the liquid.

The value of 18.2 dynes cm^{-1} for the surface tension of vanadium pentafluoride at 25° is lower than the values for all associated fluorides[6]. This is surprising, since in the associated fluorides, viscosity and surface tension decrease in the same order; $SbF_5 > BrF_3 > IF_5 > BrF_5 > ClF_3$. While the viscosity of vanadium pentafluoride falls between those of antimony pentafluoride and bromine trifluoride, the surface tension is less than that of chlorine trifluoride. The high viscosity of vanadium pentafluoride may have led to a false result for the surface tension, since for antimony pentafluoride reliable values for the surface tension could not be obtained by capillary rise methods[8] and it was found necessary to use the maximum bubble pressure method. If this were so for vanadium pentafluoride, then it is surprising that two different capillary rise methods should give results in such good agreement.

The molar surface energy T, given by the equation $T = \gamma(Mv)^{2/3}$ where γ is the surface tension, M is the molecular weight and v is the specific volume, was calculated for vanadium pentafluoride and plotted against temperature. Hence the Eötvos

coefficient $(\frac{d\Gamma}{dt})$ was found to be -1.9, as compared with the value of -2.1 expected for non-associated liquids. The ratio of these two values indicates that the degree of molecular association is apparently not much greater than unity. However, many associated as well as non-associated liquids yield the non-associated value for the Eötvos coefficient and little reliable information can be deduced concerning the degree of molecular association. The high viscosity of vanadium pentafluoride, which is a more reliable indication of association, means that the liquid is probably highly associated in spite of the low surface tension and normal Eötvos coefficient. The similarity of the viscosity to that of antimony pentafluoride, both of which are much more viscous than the halogen fluorides, suggests that both pentafluorides are associated into chain polymers in contrast to the dimeric species probably present in the halogen fluorides.

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Part 2.

Thermochemistry of Vanadium Tetrachloride
and the Vanadyl Ion

By R. G. Cavell and H. C. Clark

During a thermochemical study of the vanadium fluorides[1], a value for the heat of hydrolysis of vanadium tetrachloride was required for inclusion in a thermochemical cycle. Ruff and Freidrich[2] have found the heat of hydrolysis of vanadium tetrachloride, according to the equation

$$VCl_4(1)+{}^9/_2OH^-(aq)+{}^1/_2O_2H^-(aq) \longrightarrow VO_3^-(aq)+{}^5/_2H_2O+4Cl^-(aq),$$
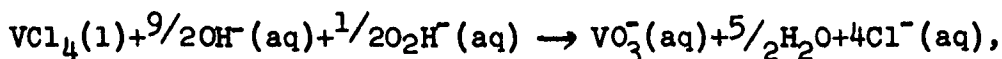
to be -161 kcal. mole^{-1}. However, this reaction was not applicable since the equation is that for hydrolysis in an alkaline peroxide solution, while the present study has been concerned with hydrolysis in distilled water. Measurements have therefore been made of the heat of hydrolysis of vanadium tetrachloride in water, and the previously unknown heat of formation of the vanadyl ion, VO^{2+}, has been calculated.

Experimental: Vanadium tetrachloride was prepared by direct chlorination of vanadium metal at 300-350°, followed by distillation of the product in an all-glass still, the fraction boiling between 152° and 154° being collected.

The calorimeter used in the determination of the heat of hydrolysis will be described elsewhere[1]. The weighed sample was contained in a glass bulb of about 3 ml. capacity with a fragile glass

tip at the bottom, and a breakseal at the top. The breakseal was sealed to a 25 cm. length of 8 mm. glass tubing, and the sample container was then inserted into the hollow shaft of the calorimeter stirrer so that the top of the long 8 mm. tube emerged from the hollow shaft. The bulb containing the vanadium tetrachloride was then immersed in the calorimeter vessel which contained a tared amount of water, and the system was allowed to reach thermal equilibrium. A slight pressure of nitrogen was applied through the 8 mm. tube, the breakseal was broken, and by jerking the sample tube upwards against the end of the stirrer shaft, the fragile tip of the sample bulb was broken. After the nitrogen pressure had forced the tetrachloride into the water, the pressure was released so that water flowed back into the sample container to remove any last traces of the tetrachloride.

Four determinations of the heat of hydrolysis were made. The specific heat of each resultant vanadyl chloride solution was determined immediately after the hydrolysis experiment and the average value for six determinations, 0.980 ± 0.005 cal. g^{-1} deg^{-1}, was used in the subsequent calculations. The solutions were analysed after each experiment and the results were in satisfactory agreement with the theoretical value of 26.4% vanadium expected for vanadium tetrachloride.

	Wt. VCl_4 (g.)	Wt. water (g.)	Water Equiv. cal. deg^{-1}	$\triangle T$ ($^{\circ}$C)	Heat liberated by wt. of VCl_4 (cal.)	Heat lib. per mole VCl_4 (cal.)
1	2.5098	900.0	99.0	0.899	884.1	67,994
2	2.3686	900.0	95.3	0.858	840.5	68,488
3	2.5000	900.0	95.3	0.903	884.7	68,302
4	2.0053	900.0	95.3	0.740	724.9	69,650

The average heat of hydrolysis of vanadium tetrachloride is
$\Delta H_{hyd.}$ = -68,630 cal. mole^{-1} with a standard deviation of
± 440 cal. Unevaluated errors probably double this error, hence
the results are considered reliable to ± 1000 cal. Heats of
solution have not been corrected to infinite dilution, but such
correction would contribute not more than 0.1 kcal. mole^{-1}.

Discussion:

Assuming that the hydrolysis of vanadium tetrachloride in
water proceeds according to the equation:

$$VCl_4(l) + H_2O(l) \longrightarrow VO^{2+}(aq) + 2H^+(aq) + 4Cl^-(aq),$$
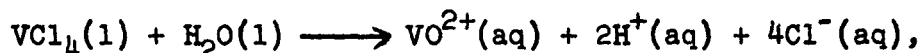
the heat of this reaction can be combined with the standard heat
of formation of vanadium tetrachloride[3], and with other thermo-
chemical data[4], to complete the thermochemical cycle giving the
standard heat of formation of the $VO^{2+}(aq)$ ion. The heat of form-
ation of the vanadyl ion at 298°K is: $\Delta H_f o(VO^{2+}(aq))$ = -113
± 1 kcal. mole^{-1}. The standard free energy of formation of
$VO^{2+}(aq)$ obtained from measurements of electrochemical cell
potentials[5] is: $\Delta G_f o(VO^{2+}(aq))$ = -109 kcal. mole^{-1}. Hence the
entropy change of formation, $\Delta S_f o$, has a value of -13.4 e.u.
at 298°K. The corresponding value for the vanadate ion is not
known, so comparisons are not possible.

By addition of the equation for the hydrolysis of vanadium
tetrachloride in an alkaline peroxide solution[2] to the reverse of
the equation for the present hydrolysis reaction, the equation

$$VO^{2+}(aq) + \tfrac{5}{2}OH^-(aq) + \tfrac{1}{2}O_2H^-(aq) \longrightarrow VO_3^-(aq) + \tfrac{7}{2}H_2O(l)$$
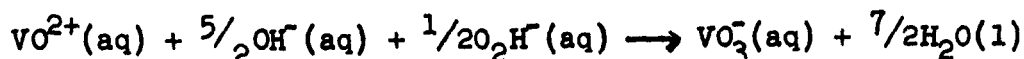
is obtained. This represents the oxidation of tetravalent vanadium to quinquevalent vanadium in alkaline peroxide solution, and $\triangle H$ for this reaction is -92.4 kcal. mole^{-1}.

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Part 3.

The Thermochemistry of Vanadium Fluorides

by R. G. Cavell and H. C. Clark

ABSTRACT

The heat of hydrolysis of vanadium tetrafluoride in water
has been found to be -27.5 kcal/mole, and hence the heat of
formation is calculated to be -331.8 ± 1.5 kcal/mole. Vanadium
pentafluoride, hydrolysed in dilute sodium hydroxide solution,
gave a heat of hydrolysis of -141.3 kcal/mole, and hence the heat
of formation is -352 ± 3 kcal/mole. Lattices energies have been
estimated for trifluorides and tetrafluorides of some transition
metals using the Kapustinskii formula, and have been used to
calculate heats of formation. The thermodynamic stabilities of
the fluorides of vanadium, and of some other transition metal
tetrafluorides are then discussed. Mean bond dissociation energy
values have been calculated for the vanadium fluorides.

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Of the three simple fluorides of vanadium, the tetrafluoride
and the pentafluoride have only recently been studied in any
detail[1,2]. Ruff and Lickfett's[3] earlier observation of the
disproportionation at 325°C of vanadium tetrafluoride into the
trifluoride and pentafluoride has been confirmed; indeed, it has
been shown[2] that the disproportionation occurs slowly but spon-
taneously at room temperature. Since such disproportionations are

rare among the metal fluorides, it was of some interest to study the thermochemistry of these fluorides and hence examine their thermodynamic stabilities.

Experimental:

Vanadium tetrafluoride and pentafluoride were prepared and manipulated as previously described[1,2].

(a) The calorimeter: A solution calorimeter was constructed from a simple Parr bomb calorimeter. The metal internal vessel and bomb assembly were replaced with a 1 litre polyethylene vessel and a hollow shaft brass stirrer. The stirrer was driven electrically using a belt drive to minimise heat transfer to the stirrer, and was fitted through polyethylene bearings on the lid of the calorimeter to obtain smooth stirring with minimum friction. Both the depth of immersion of the stirrer, and the position of the stirrer blades on the shaft could be independently adjusted.

An eight ohm heater, consisting of nichrome wire wound about a polyethylene tube, was immersed in the plastic calorimeter vessel. In determining the water equivalent of the system, the bare wires could be exposed to water without effect, however in vanadium fluoride solution, passage of current caused electrochemical corrosion of the nichrome wire which changed the resistance of the heater. A thin coating of paraffin wax applied to the heater wire prevented the corrosion with only slight effect on the heat transfer to the solution. Current was supplied to the heater from a freshly charged 12 volt lead storage cell, and was measured by determining the potential difference across an accurately measured standard resistor of manganin wire.

The temperature was measured with a standard Beckmann thermometer, graduated to $0.01^{\circ}C$. Since the presence of glass in the vanadium fluoride solutions was undesirable, the immersed part of the thermometer was thinly coated with paraffin wax. This was sufficient to prevent attack by hydrofluoric acid but had little effect on the thermal response of the thermometer.

Because a slightly different sample delivery system was used for each compound studied, the water equivalent had to be determined for each system. Typically, a known amount of heat (Q) was delivered to the calorimeter by means of the heater coil, and the increase in temperature was measured. From a time-temperature graph, a correction was made for heat losses during the heating, and the water equivalent (WE) was calculated from the expression $WE = \dfrac{Q - (Ws\,\triangle T)}{T}$ where Q is the heat applied in calories, W the weight of water in grams, s the specific heat of the solution, and $\triangle T$ the temperature change in $^{\circ}C$. A constant weight of water was used for every measurement of the water equivalent, heat of hydrolysis, and specific heat of the resultant solution. The specific heat was determined by the same procedure for each solution immediately after the hydrolysis of the vanadium compound.

(b) Heat of hydrolysis of Vanadium Tetrafluoride: The sample holder designed for powdered solids such as vanadium tetrafluoride is shown in the figure. It consisted of a 13 mm. diameter brass tube approximately 6 cm. long, which could be screwed into the base of the hollow shaft of the stirrer. A 0.01 mm. Parafilm "M" (Marathon Chemical Co.) diaphragm was sealed to the bottom of the container by means of a wide, threaded flange and compression nut. A

close-fitting polyethylene plug, fitted with a sharp spike for piercing the diaphragm, was inserted in the top, leaving a completely enclosed sample volume of about 3 ml.

A typical determination was made as follows. A carefully weighed amount of the tetrafluoride was inserted in the sample holder in the dry box. The sample container was then screwed to the stirrer shaft and immersed in a weighed amount of water in the calorimeter vessel. After thermal equilibrium had been attained, the polyethylene plug and spike were pushed through the diaphragm forcing all of the solid into the water. When the plug left the holder, the solution washed the inner walls of the container free of any adhering vanadium tetrafluoride, thus ensuring complete solution of the sample. The solutions were titrated for vanadium (IV) with standard potassium permanganate after each experiment and the results confirmed that all the vanadium had dissolved as vanadium (IV). The final solution temperature after each hydrolysis was within 0.2° of $25.0^{\circ}C$.

(c) Heat of Hydrolysis of Vanadium Pentafluoride: The figure also shows the sample holder designed for vanadium pentafluoride which is a highly reactive liquid at 25°. The sample was contained in an approximately 2 ml. cylindrical stainless steel chamber, 6 mm. internal diameter and 30 mm. in length, which was attached to a 13 cm., 4 mm. diameter, thin-walled stainless steel tube. A platinum diaphragm, 0.002 mm thick, was welded to the bottom of the sample chamber to provide a vacuum tight seal. Below the platinum diaphragm, a small sharp spike was mounted vertically on a nichrome frame as shown in the figure. The top of the long stainless steel tube was

welded to a Kovar-Pyrex graded seal, the glass end of which was
sealed to a break seal and a capillary constriction inlet. The
sample holder was connected to the vanadium pentafluoride supply
by a B-10 ground-glass joint attached to the capillary constriction.
The joint was sealed with a Teflon sleeve and an inner tube passed
through the joint to minimise contact of the pentafluoride with the
glass joint.

The weighed sample holder was evacuated and carefully dried.
About 1 g. of vanadium pentafluoride was distilled into the sample
holder, which was then sealed off at the capillary constriction and
reweighed. The sample holder was suspended in the calorimeter
vessel, through the hollow shaft of the stirrer, and, with standard
sodium hydroxide solution in the calorimeter vessel, the system was
allowed to come to thermal equilibrium.

A slight pressure of dry nitrogen was applied to the top of
the sample holder, and the break-seal was broken. The sample holder
was then gently forced down on to the sharp spike, rupturing the
platinum diaphragm and allowing the nitrogen to force the vanadium
pentafluoride into the sodium hydroxide solution. By the alternate
application of a slight suction and a nitrogen pressure to the
sample holder, the metal part of the sample holder was thoroughly
rinsed with the hydroxide solution, thus hydrolysing any adhering
pentafluoride. Temperature measurements were taken at one minute
intervals for several minutes before and after hydrolysis, and
the temperature rise on hydrolysis was corrected for heat losses
to the surroundings.

The normality of the resultant alkaline vanadate solutions was determined by titrations with standard hydrochloric acid, and the corresponding amount of vanadium pentafluoride dissolved was calculated according to the equation:

$$VF_5(l) + 6OH^-(aq) \longrightarrow VO_3^-(aq) + 5F^-(aq) + 3H_2O.$$
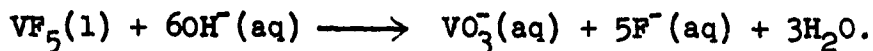
The solutions were also analysed for vanadium, the results agreeing with the expected concentrations for vanadium pentafluoride. Titration of the vanadate solutions immediately after hydrolysis indicated no detectable amounts of reduced species such as tetravalent vanadium.

A small difference between the actual weight of vanadium pentafluoride taken and the weight calculated from the consumption of alkali according to the above equation was found in three experiments. This discrepancy may be due to further hydrolysis of the metavanadate, VO_3^-, ion to species such as $HV_2O_7^{-3}$ or VO_4^{-3} etc. which increases the hydroxide consumption and thus increases the apparent weight of VF_5 involved. The magnitudes of the differences indicate that less than 1.5% of the vanadium is involved in further hydrolysis and in any case there does not appear to be a distinct correlation between the amount of excess hydrolysis and the heat of hydrolysis. Any thermochemical effects due to this cause are probably included in the deviation limits. The lack of thermochemical data for vanadate species other than VO_3^- necessitates the simplifying assumption that VF_5 hydrolyses to VO_3^- and the analyses indicate that this is largely so.

Results:

(a) Heat of Hydrolysis of Vanadium Tetrafluoride

The water equivalent in the following experiments was 49.5 ± 0.5 cal./deg, and the specific heat, determined in two runs on each solution, gave an average value (eight runs) of 0.985 ± 0.002 cal./gm. deg.

Expt. No.	Wt. VF_4 (gm)	Wt. Water (gm)	$\Delta T(^{o}C)$	$-\Delta H$ for wt. of VF_4 (cal.)	$-\Delta H$ (cal/mole)
1	2.7763	956.2	0.601	597.45	27,330
2	2.3875	956.2	0.522	518.74	27,593
3	2.1476	956.2	0.471	467.92	27,671
4	2.3376	956.2	0.509	505.77	27,476

The average heat of hydrolysis of vanadium tetrafluoride is $-\Delta H_{hyd.}$ = 27,520 cal./mole, the standard deviation shown by these results being ± 120 cal. Considering the effect of unknown errors, the results are to be considered reliable to within ± 0.5 kcal./mole or ± 1.5%.

(b) Heat of Hydrolysis of Vanadium Pentafluoride

The water equivalent was 79 ± 1 cal./deg., and the specific heat of each of the solutions was determined to give an average value of 0.978 ± 0.005 cal./gm. deg. The final solution temperature after each hydrolysis was within 0.2°C of 24.5°C.

Expt. No.	1	2	3	4
Wt. NaOH soln (g.)	900.0	900.0	897.0	900.0
Wt. VF_5(g.)	0.9993	0.9971	1.0891	1.1552
Wt. VF_5 (g.) calc. from normality change	1.05	1.07	1.12	1.15
$\triangle T$ ($^\circ$C)	1.000	1.014	1.110	1.145
Heat evolved by wt. of VF_5 (cal.)	960.18	973.62	1062.65	1099.58
Heat evolved per mole VF_5 (cal.)	140,280	142,560	142,455	138,970

The average heat of hydrolysis is $-\triangle H_{hyd.} = -141,100$ cal/mole, the standard deviation of the results being $\pm$ 1,750 cal. The larger error in the heat of hydrolysis of vanadium pentafluoride, as compared with that for vanadium tetrafluoride, reflects the greater experimental difficulties encountered in the manipulation of a reactive volatile liquid. Allowing for unknown sources of error the results are probably reliable to within $\pm$ 3 kcal. or about $\pm$ 2%.

Discussion:

(a) The Standard Heat of Formation of Vanadium Tetrafluoride. The hydrolysis of vanadium tetrafluoride in distilled water likely proceeds according to equation 1,

1. $VF_4(s) + H_2O \longrightarrow VO^{2+}(aq) + 4F^-(aq) + 2H^+(aq) + 27.5$ kcal.
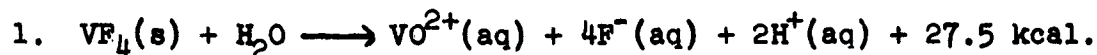
and the experimental data gives the average heat evolved during this hydrolysis as -27.5 ± 0.5 kcal./mole. The thermochemical cycle for the heat of formation was completed by combining reaction 1 with the following reactions:

Reaction	kcal/mole	Reference

2. $VO^{2+}(aq) + 2H^+(aq) + 4Cl^-(aq)$

   $\longrightarrow VCl_4(1) + H_2O$ (1)   -68.6   4

3. $VCl_4(1) \longrightarrow V(s) + 2Cl_2(g)$ -136.2   5

4. $2Cl_2(g) \longrightarrow 4Cl^-(aq)$ +160.1   6

5. $4F^-(aq) \longrightarrow 2F_2(g)$ -314.6   6

Adding reactions 1 - 5 gives

$$VF_4(s) \longrightarrow V(s) + 2F_2(g) - 331.8$$
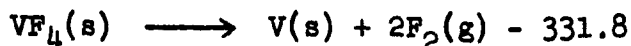
This is the reverse of the formation reaction of vanadium tetra-fluoride and therefore $- \Delta H_f o(VF_4) = 331.8$ kcal/mole. The standard heats of formation at $298^\circ K$ of the ions are the values for each ion at infinite dilution. The error arising from this approximation is no greater than 0.1 kcal/mole and is insignificant in the present study. The only errors estimated are those arising from experimental heats of hydrolysis of the tetrafluoride and the tetrachloride, giving an overall error of ± 1.5 kcal./mole. Reaction 2 was chosen as the most feasible method of completing the thermochemical cycle, since it is then only necessary to assume that vanadium tetrafluoride and vanadium tetrachloride hydrolyse to the same cationic species under similar conditions, rather than specifically assuming hydrolysis to VO^{2+}.
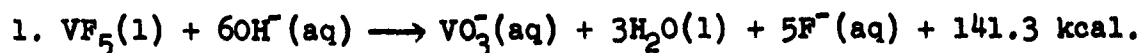
(b) The Standard Heat of Formation of Vanadium Pentafluoride. Vanadium pentafluoride hydrolyses in dilute alkaline solution largely according to the equation:

1. $VF_5(1) + 6OH^-(aq) \longrightarrow VO_3^-(aq) + 3H_2O(1) + 5F^-(aq) + 141.3$ kcal.

The thermochemical cycle for the heat of formation of vanadium pentafluoride was completed by combining reaction 1 with the following reactions[6].

Reaction	kcal./mole
2. $VO_3^-(aq) \longrightarrow V(s) + ^3/_2O_2(g)$	-224.5
3. $3H_2(g) + 3O_2(g) \longrightarrow 6OH^-(aq)$	+329.5
4. $3H_2O(l) \longrightarrow 3H_2(g) + ^3/_2O_2(g)$	-204.96
5. $5F^-(aq) \longrightarrow ^5/_2F_2(g)$	-393.3

Adding reactions 1-5, gives $- \Delta H_f o(VF_5(l)) = 351.9$ kcal/mole. As before, the largest error is that arising from the experimental determination of the heat of hydrolysis, probably about $\pm$ 3 kcal./mole. The standard heat of formation is, therefore, $- \Delta H_f o(VF_5(l)) = 352 \pm$ 3 kcal./mole.

(c) Theoretical estimation of Heats of Formation.

Theoretically, the heat of formation of an ionic solid such as a metal fluoride can be calculated from the expression.[8]

$$\Delta H_f o \ (MF_n) = \sum_n I_1 + L - n(E - ^D/_2) - U,$$

where $\sum_n I_1$ represents the sum of the successive n ionisation potentials[9] of the metal M, E is the electron affinity of fluorine, and D the enthalpy of dissociation of fluorine, L the enthalpy of sublimation[10] of the metal, and U is the lattice energy of MF_n. Since all the quantities except the lattice energy, U, are readily available, the problem of calculating the heat of formation becomes one of evaluating the lattice energy. Although exact lattice energy calculations are lengthy and involved, values can be obtained in a

simple manner by applying the Kapustinskii formula[7,8]

$$U = \frac{287.2\ vz_A z_c}{r_A + r_c} \left[1 - \frac{0.345}{r_A + r_c} \right] \quad ,$$

where z_A and z_c are the anionic and cationic charges respectively, r_A and r_c are the anionic and cationic radii respectively, and v is the number of ions in a formula unit of the compound. The lattice energies for a series of tri- and tetrafluorides of the first long period transition metals and for zirconium tetrafluoride have been estimated with this formula. By substituting these results into the above equation the heats of formation of the fluorides have been calculated. The ionic radii used were Pauling's[11] crystal radii which yield close agreement with measured interatomic distances in these fluorides. Where such radii were not available (e.g. for iron and cobalt) empirical crystal radii[11] or ionic radii were used; where the ionic radii were extremely uncertain, i.e. for Mn^{4+}, upper and lower limits were assigned to the radii and hence to the lattice energy and heat of formation, following the practice of Barker, Linnett and Taylor[16]. The resulting values of the lattice energies, heats of formation, and experimentally observed heats of formation are shown in Table 1. The references given are those for the experimental heats of formation.

Table 1

Element Trifluorides	r^{n+} (A)	U(MFn) kcal/mole	$\Delta H_f(MF_n)$ (kcal/mole) Calc.	Obs.	Ref.
Ti	0.73	1376	-345	-315	6
V	0.67	1409	-319	-	
Cr	0.64	1426	-281	-265	12
Mn	0.62	1438	-261	-238	13
Fe	0.60	1449	-288		
Co	0.63	1432	-183	-187	6
Tetrafluorides					
Ti	0.68	2339	-385	-394	14
V	0.65	2413	-315	-332	Present worl
Cr	0.56	2454	-233	-287	12
Mn	0.54-0.60	2474-2415	-165 to -105	-	
Zr	0.80	2234	-536	-457	15
Fe	0.52-0.60	2494-2414	-246 to -167	-	
Co	0.50-0.60	2516-2414	-180 to -79	-	

Considering the approximate nature of the lattice energy calculations, the agreement between experimental and calculated heats of formation is surprisingly good. This indicates that calculated values of the heats of formation may be used when experimental values are not available as in the case of vanadium trifluoride.

The discrepancies between experimental and calculated values are probably due to errors in the lattice energy estimation. The Kapustinskii formula appears to overestimate the lattice energies of the trifluorides, and to underestimate the lattice energies of

the trifluorides, and to underestimate the lattice energies of the
tetrafluorides, of the elements of the first long period, probably
because of the increase in covalent character of the M-F bonds
accompanying the increased valence. Effectively the Kapustinskii
formula arbitrarily compensates for a constant amount of covalent
character, whereas in fact covalent character changes with valence
and ionic size.

Barber, Linnett and Taylor[16], using a much more approximate
formula for the lattice energy, have also calculated heats of
formation for the trifluorides of the first long period elements.
In general, their results were about 100 kcal./mole greater than the
present calculated values, and thus showed poorer agreement with the
experimental values. Their more approximate method, which was used
to calculate heats of formation of mono-, di-, and trihalides of
the transition metals of the first long period, yielded heats of
formation which showed good agreement with experimental values
only for the chlorides. That the present calculations give good
agreement for fluorides, suggests that such agreement with
experimental values is obtained fortuitously rather than from a
complete evaluation of the lattice energy through a valid
theoretical expression.

(d) Thermodynamic Stability of Vanadium Fluorides.
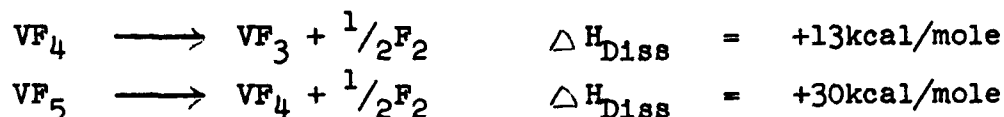
Consider first the disproportionation $2VF_4 \longrightarrow VF_5 + VF_3$.
The heat of the disproportionation reaction, $\triangle H_D$, is given by the
expression $\triangle H_f o(VF_5) + \triangle H_f o(VF_3) - 2\triangle H_f o(VF_4)$, and by applying
the experimental heats of formation for the tetra- and penta-
fluorides, and the calculated value for the trifluoride, a value of

-7 kcal./mole is obtained. If $\triangle H_D$ be considered an approximate criterion, then the disproportionation reaction is spontaneous. Moreover, since the reaction produces a gaseous product, $\triangle S_D$ is probably positive, so that $\triangle G_D$ will have a greater magnitude than $\triangle H_D$, thus confirming the spontaneity. This is in accord with the observed rapid disproportionation according to the above equation[2].

Similarly, values can be calculated for the heats of dissociation of the tetrafluoride and pentafluoride.

$$VF_4 \longrightarrow VF_3 + \tfrac{1}{2}F_2 \qquad \triangle H_{Diss} = +13\text{kcal/mole}$$
$$VF_5 \longrightarrow VF_4 + \tfrac{1}{2}F_2 \qquad \triangle H_{Diss} = +30\text{kcal/mole}$$

Both modes of dissociation are, therefore, extremely unlikely and there is no experimental evidence to suggest that either dissociation reaction occurs.

(e) Thermodynamic Stability of Tetrafluorides of First Period Transition Metals.

Further, it is of interest to consider the thermodynamic stability of the tetrafluorides, particularly with respect to the dissociation $MF_4 \longrightarrow MF_3 + \tfrac{1}{2}F_2$. The required heats of formation are taken from Table 1, using both calculated and experimental values, and the resulting heats of reaction are shown in Table 2. The lack of the necessary ionisation potentials and ionic radii prevents the evaluation of heats of reaction for the disproportionation $2MF_4 \longrightarrow MF_5 + MF_3$.
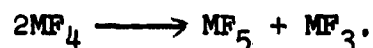
The results are quite striking. The heats of dissociation of the tetrafluorides of titanium, vanadium, and chromium into the

trifluorides are either quite endothermic or almost zero, particularly
if the available experimental values are chosen in preference to
calculated heats of formation. The latter give values which suggest

Table 2.

$$MF_4 \longrightarrow MF_3 + {}^{1}\!/_2 F_2$$

		ΔH kcal/mole			ΔH kcal/mole
Ti	Calc.	+40	Mn	calc.	-96 to -156
	exptl.	+78		exptl.*	-53 to - 33
V	calc.	- 4	Fe	calc.	-42 to -121
	exptl.	+13			
Cr	calc.	-48	Co	calc.	- 3 to -104
	exptl.	+22		exptl.*	- 7 to -108

* Using calculated value for $\Delta H_f o$ (MF_4)

that the dissociation reactions are more feasible than actually
observed. For the tetrafluorides of Mn, Fe, and Co, the reactions
become highly exothermic, and these tetrafluorides will show a
strong tendency to dissociate into the trifluorides and fluorine.
Iron and cobalt tetrafluorides have not yet been prepared; manganese
tetrafluoride has recently been prepared and does indeed dissociate
into the trifluoride and fluorine[17].

(f) Bond Energies of Vanadium Fluorides

From the calculated heat of formation for vanadium trifluoride
and the experimental heats of formation for the tetrafluoride and
pentafluoride, the mean bond energy of the V-F bond in each of these
compounds has been calculated. The values obtained are 166 $\pm$

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</div>

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10 kcal/mole for V-F in VF_3, 132 kcal/mole in VF_4 and 114 kcal/mole in VF_5. These may be compared with mean bond dissociation energies in other metal fluorides, calculated from the experimental values of the heat of formation given in the accompanying references. The mean M-F bond dissociation energy is 142 kcal/mole for NbF_5[18], 145 kcal/mole for TiF_4[14] and 169 kcal/mole for ZrF_4[15]. The bond energies of the vanadium fluorides may also be compared with the values of 144 kcal/mole in VCl_2[6], 115 kcal/mole in VCl_3[6] and 93 kcal/mole in VCl_4[5], also calculated from the heats of formation given in the references.

The increase in bond energy of approximately 40% from chloride to fluoride of the same valence follows the probable increase of ionic character of the metal-halogen bond. Similarly, the decrease in bond energy with increasing valence of the metal in both chloride and fluoride series parallels the expected decrease in ionic character of the metal halogen bond.

The reliability of the preceding thermodynamic calculations for the vanadium fluorides would be greatly increased by an experimental determination of the heat of formation of vanadium trifluoride. Unfortunately the heat of hydrolysis cannot be measured as for the tetra- and penta-fluorides, because of the very low dissolution of the trifluoride in water. Fluorine bomb calorimetry could not be applied since under the necessary conditions the higher fluorides would probably be formed. The reaction of vanadium metal with hydrogen fluoride in a bomb calorimeter could possibly be studied since only vanadium trifluoride is formed[19], however some improvement of the yield would be necessary.

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